U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB80-118763

Further Characterization of Sorbents for Environmental Sampling

Arthur D. Little, Inc, Cambridge, MA

Sep 79

PB80-118763

United States
Environmental Protection
Agency

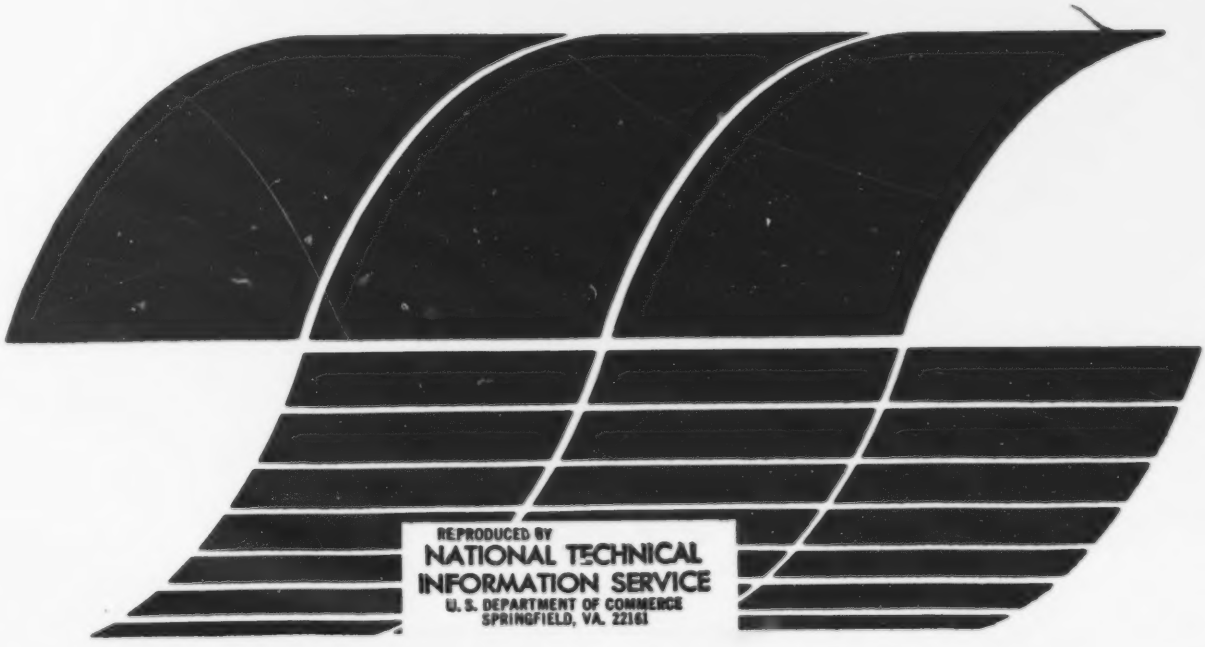
Industrial Environmental Research
Laboratory
Research Triangle Park NC 27711

EPA-600/7-79-216
September 1979

EPA

Further Characterization of Sorbents for Environmental Sampling

Interagency Energy/Environment R&D Program Report



REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the INTERAGENCY ENERGY-ENVIRONMENT RESEARCH AND DEVELOPMENT series. Reports in this series result from the effort funded under the 17-agency Federal Energy/Environment Research and Development Program. These studies relate to EPA's mission to protect the public health and welfare from adverse effects of pollutants associated with energy systems. The goal of the Program is to assure the rapid development of domestic energy supplies in an environmentally-compatible manner by providing the necessary environmental data and control technology. Investigations include analyses of the transport of energy-related pollutants and their health and ecological effects; assessments of, and development of, control technologies for energy systems; and integrated assessments of a wide range of energy-related environmental issues.

EPA REVIEW NOTICE

This report has been reviewed by the participating Federal Agencies, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Government, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/7-79-216		PB80-118763

4. TITLE AND SUBTITLE	5. REPORT DATE
Further Characterization of Sorbents for Environmental Sampling	September 1979
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
J.F. Piecewicz, J.C. Harris, and P.L. Levins	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Arthur D. Little, Inc. Acorn Park Cambridge, MA 02140	EHB 537
	11. CONTRACT/GRANT NO.
	68-02-2150, T.D. 10601
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
EPA, Office of Research and Development **Industrial Environmental Research Laboratory** **Research Triangle Park, NC 27711**	Final; 3/78 - 6/79
	14. SPONSORING AGENCY CODE
	EPA/600/13

15. SUPPLEMENTARY NOTES IERL-RTP project officer is Larry D. Johnson, Mail Drop 62, 919/541-2557.

16. ABSTRACT The report gives results of an ongoing experimental program to evaluate the breakthrough characteristics of sorbent resins for sampling of organic vapors using an elution analysis chromatographic technique. The effects of water vapor and CO_2, at levels typical of gaseous effluents from combustion processes, on retention of nonpolar and polar species on two commonly used sorbents (XAD-2 and Tenax-GC) have been studied. Effects on XAD-2 were small but the volumetric capacity of Tenax-GC was substantially decreased. Other sorbents were characterized for potential use in vapor sampling systems: coconut-based charcoal, petroleum-based charcoal, silica gel, Ambersorb XE-340 and XE-347, and XAD-8. Retention volumes for XAD-8 and silica gel were roughly comparable to those of XAD-2 and Tenax-GC; those of the charcoals and the Ambersorbs were 2 to 4 orders of magnitude higher. Recovery of sorbate from charcoals is known to be poor in some cases, however, and recovery from the Ambersorbs is suspect but under investigation.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Pollution Control	13B
Sampling	Stationary Sources	14B
Sorbents	Resins	11G
Polymers	XAD-2	07D
Organic Compounds	XAD-8	07C
Carbon Dioxide	Tenax-GC	07B
Charcoal	Ambersorbs	21D
Analyzing		
Vapors		
Chromatography		
Water Vapor		
Silica Gel		

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
Release to Public	**Unclassified**	47
	20. SECURITY CLASS (This page)	22. PRICE
	Unclassified	PC-A03/MF-A01

EPA Form 2220-1 (9-73)

EPA-600/7-79-216

September 1979

Further Characterization of Sorbents for Environmental Sampling

by

J. F. Piecewicz, J. C. Harris, and P. L. Levins

Arthur D. Little, Inc.
Acorn Park
Cambridge, MA 02140

Contract No. 68-02-2150
T. D. No. 10601
Program Element No. EHB537

EPA Project Officer: Larry D. Johnson

Industrial Environmental Research Laboratory
Office of Environmental Engineering and Technology
Research Triangle Park, NC 27711

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, DC 20460

TABLE OF CONTENTS

		Page
LIST OF FIGURES		iv
LIST OF TABLES		v
I.	SUMMARY	1
II.	INTRODUCTION	2
III.	BACKGROUND	4
IV.	APPROACH	6
	A. Experimental Technique	6
	B. Experimental Apparatus	7
	C. Introduction of Sorbate Samples	13
	D. Materials and Reagents	13
	E. Matrix of Experiments	15
V.	RESULTS	18
	A. Effects of Major Combustion Gases	18
	B. Comparison of Various Sorbents	22
VI.	CONCLUSIONS AND RECOMMENDATIONS	35
VII.	REFERENCES	36
APPENDIX A		A-1

LIST OF FIGURES

Figure No.		Page
1	Relationship Between Initial Retention Volume V_I and V_g^T	8
2	Gas Chromatographic Apparatus Used to Determine V_g^T	9
3	Moisture Generation System	11
A-1	Incremental Surface Area Distribution (Desorption) XE-340	A-2
A-2	Incremental Surface Area Distribution (Desorption) XE-347	A-3
A-3	Incremental Surface Area Distribution (Desorption) XAD-8	A-4
A-4	Incremental Surface Area Distribution (Desorption) Charcoal Lot 104	A-5
A-5	Incremental Surface Area Distribution (Desorption) Charcoal Lot 106	A-6

LIST OF TABLES

Table No.		Page
1	Sorbates and Suppliers Used in the Study	14
2	Sorbents and Suppliers Used in the Study	14
3	Experimental Matrix - Combustion Gas Studies	16
4	Experimental Matrix - Other Sorbent Studies	17
5	% Relative Humidity Compared to Column Temperature at constant 10% Moisture (vol/vol)	18
6	Comparison of V_g for Dry and Low % Relative Humidity Atmospheres in XAD-2	19
7	Comparison of V_g's for Sorbates at Two Different Relative Humidities on XAD-2	20
8	Comparison of V_g's for Sorbates at Two Different Relative Humidities on Tenax-GC	21
9	Comparison Data for V_g in Humid Atmospheres With and Without Carbon Dioxide	23
10	Retention Volumes, V_g, on Charcoals Lots 104 and 106 for the Tested Sorbates	25
11	Comparison of Retention Volume, V_g, of the Charcoals Lots 104 and 106 at Common Temperatures	26
12	Retention Volumes, V_g, on Silica Gel for the Tested Sorbates	26
13	Retention Volumes, V_g, on the Ambersorbs XE-340 and XE-347 for the Tested Sorbates	28
14	Comparison of Sorbents via the Retention Volumes of the selected Sorbates at 20°C	29
15	Retention Volumes on XAD-8 of the Tested Sorbates	30
16	Specific Surface Areas, A_g^o, for Sorbents	32
17	Adsorption Coefficients, K_A, on Resins at 20°C	33

I. SUMMARY

In this work, elution chromatography was successfully used to study the effects of combustion gases, carbon dioxide, water and the combined effect of carbon dioxide and water on the retention volume of trace level sorbates on XAD-2 and Tenax-GC. The retention behavior of XAD-2 is relatively unaffected by the combustion gases studied. Introduction of water vapor led to V_g reductions of 0-4% for the non-polar sorbates studied and 13-17% for the two polar sorbates. Carbon dioxide at 10% (vol/vol) levels resulted in essentially no further decrease for XAD-2. On the other hand, the V_g values on Tenax-GC were reduced by 22-43% in the presence of water vapor, and an additional 25% decrease was observed when carbon dioxide was introduced.

Other sorbents have been investigated for collecting of volatile and polar organics. The charcoals, Lot 104 and Lot 106, and the Ambersorbs, XE-340 and XE-347, appear to be potential candidates for this purpose. The charcoals and Ambersorbs show V_g values three to five orders of magnitude higher than XAD-2 for non-polar sorbates. For alcohols, the differences are one to three orders of magnitude. The increased V_g's are only partially attributable to differences in surface area. Based on this study, the order of preference in selection of sorbents for collection of high volatile and polar organics, listed in order of decreasing intrinsic affinity (K_A), are: Charcoal Lot 104 > Ambersorb XE-340 > Charcoal Lot 106 > Ambersorb XE-347 > XAD-8 > Tenax-GC > XAD-2.

II. INTRODUCTION

In the past decade adsorbent-filled cartridges have found increased use in the sampling of volatile and relatively non-volatile organic compounds. This technique has been used for the study of source emission levels, ambient air concentration levels and for the characterization of occupational exposure. Sorbent sampling methods have been developed for the characterization of both air and water media. The use of sorbents for characterization of source emissions and, in general, for environmental assessment studies, has been adopted by the Process Measurements Branch by incorporation of a sorbent module in the EPA SASS train. In support of this application, and in order to provide an extended quantitative data base to guide in the application of this methodology, Arthur D. Little, Inc., has been carrying out research in this area for several years. This report represents the third in a series related to the use of sorbents for environmental sampling. The first report[1] covered a discussion of selection criteria used in choosing particular sorbents for application and presented some preliminary quantitative evaluation data for a variety of sorbents. The second report[2] presented a detailed study of the behavior of Tenax-GC and XAD-2 for a variety of sorbents. That report demonstrated that a good correlation existed between the elution volume of a sorbate on a sorbent (V_g^T) and physical properties such as boiling point. The correlations generally were grouped by chemical class type.

These quantitative studies have demonstrated that elution chromatography is an efficient means of providing quantitative data necessary to make the evaluation and selection of the proper conditions for use of sorbents in a variety of sampling applications. At the conclusion of the latter study, several additional areas of research were identified. These included:

1) A study of the effects of major combustion gases, water and carbon dioxide, on the elution characteristics of sorbents.
2) Evaluation of other sorbents which might be more effective

in the collection of more volatile species and more polar chemical groups.

3) A study of the effect of other types of major components on the elution characteristics of sorbents. An example would be the effect of methane in a gasifier sampling stream.
4) A study of other sorbates such as organometallics.

The material in this report deals with items (1) and (2) listed above. Studies of combustion gas effects have been continued on both Tenax-GC and XAD-2. Each of these resins has particular value for special sampling and analysis applications. Studies of other sorbents have involved the following: charcoal Lot 104 and Lot 106, silica gel, ambersorb XE-340 and XE-347, and XAD-8.

III. BACKGROUND

Sorbent modules are frequently employed as one of a number of collection devices or stages in a multi-purpose sampling device, such as the EPA-SASS train.[3] The SASS train sorbent trap is primarily designed to capture organic species that have sufficient volatility to pass through particulate filters upstream from the sorbent bed.

For several reasons, care must be taken in designing experiments and interpreting results with sorbent traps. Very volatile gases are retained poorly by most sorbent resins currently used in sampling devices. Other species will "break through" the trap if the sampled volume exceeds the volume or weight capacity of the sorbent.

The availability of data which describe the quantitative relationship between sorbent, chemical species and sampling volumes allows the sampling conditions to be specified so that reliable results may be obtained.

One of the more common methods of characterizing adsorbents is the use of gas chromatography. Several reviews[4,5] attest to the popularity of this technique for thermodynamic and kinetic characterization of solid surfaces. The retention time (volume) in a gas chromatography experiment is directly related to the breakthrough volume that would be observed for an organic adsorbate in a sorbent sampler. Thus, tabulations of chromatographic retention data have intrinsic value to the chemist or engineer designing a sampling experiment involving sorbent resins. These data allow an estimate to be made as to the suitability of a particular adsorbent for the source to be sampled, the time required until breakthrough has occurred, and the amount of sorbent required to collect a sufficient amount of analyte for analytical or biological testing.

The previously reported studies in this series on the subject of sorbent traps have considered:

- The retention characteristics exhibited by two specific sorbent resins, XAD-2 and Tenax-GC, for a large variety of compound types.

- Correlation of chromatographic retention volume data generated by a sorbent trap exposure apparatus with frontal analysis results.

- The relationship between the equilibrium adsorption isotherm and the retention volume results obtained in the low surface coverage region (i.e., Henry's Law region) and its application to sorbent sampling device design.

- The relationship between elution and frontal chromatographic approaches and the advantages and disadvantages of the several chromatographic-based methods for determining V_g^T, breakthrough curves (adsorption and desorption branches), adsorption isotherms, and weight capacity of the sorbent trap.

- The effect of flow rate on retention volume, particularly at face velocities similar to those corresponding to actual sampling conditions.

- The correlation of elution volume (V_g^T) data with sorbate physical properties to aid in the prediction of breakthrough volumes of other organic species.

IV. APPROACH

A. Experimental Technique

The chromatographic method used in this study was that of elution analysis. In elution analysis, a small quantity of adsorbate is injected onto the sorbate cartridge in a very short time. The specific retention volume, V_g^T, can be determined for a sorbate on a particular sorbent from the resultant elution peak.

The specific retention volume, V_g^T, is the fundamental retention constant in gas chromatography and reflects the effect of flow rate, pressure drop, temperature, column void volume, and stationary phase weight (volume or surface area) on the retention of an injected solute. Knowledge of the value of V_g^T allows one to estimate the retention volume of a solute at another temperature or for a different sorbent cartridge size. Thus, V_g^T determined from conventional gas chromatographic columns can aid in design of sorbent sampling modules.

Specific retention volumes, which actually correspond to the 50% breakthrough in an elution chromatography experiment, in this study were computed according to the following formula, which defines V_g^T at the temperature of the column oven in the chromatographic experiement. The derivation of this equation has been given elsewhere.[5]

$$V_g^T = \frac{jF_c(t_r - t_a)}{W_A}$$

Where V_g^T = specific retention volume for the adsorbate at column (sorbent trap) temperature

F_c = flow rate of carrier gas at column temperature and pressure

t_r = peak maximum retention time

t_a = retention time for a completely non-sorbed solute

W_A = adsorbent weight

j = pressure correction

The correspondence between V_g^T and the 50% breakthrough in an elution chromatography experiment is illustrated in Figure 1. The actual breakthrough of the sorbate begins to occur after V_I volumes of gas have passed over the sorbent bed. However, V_I is not routinely determined, because its value is flow rate dependent, shows a dependence on the packing structure of the sorbent column, and is difficult to precisely locate on the chromatogram. The specific retention volume V_g^T, on the other hand, is easily located and is the only point on the chromatographic band corresponding to true thermodynamic equilibrium. A safety factor can be built into any calculation of breakthrough volume to account for the disparity between V_g^T and V_I.

The specific retention volume, V_g^T, for a sorbate on a sorbent is directly related to the equilibrium adsorption coefficient, K_A, so long as the experiments are carried out a low sorbate concentrations (the Henry's Law region). Under these conditions,

$$V_g^T = K^*_A \quad A^\circ_s$$

where V_g^T = specific retention volume
K^*_A = equilibrium adsorption coefficient
A°_s = adsorbent specific surface area

B. Experimental Apparatus

Figure 2 is a schematic of the basic apparatus used to determine elution volumes, V_g^T, in this study and in work reported earlier.[2] Principal components of the apparatus are: the sorbent cartridge, the gas chromatograph, and the pressure, flow and temperature measuring systems.

The sorbent cartridges were proportionally scaled down from the typical cross-section of a SASS train sorbent resin canister. Stainless steel tubing 9 cm long, 0.45 to 0.51 cm I.D., and 0.64 cm O.D., was used to contain the resin. The sorbent cartridge was connected to two

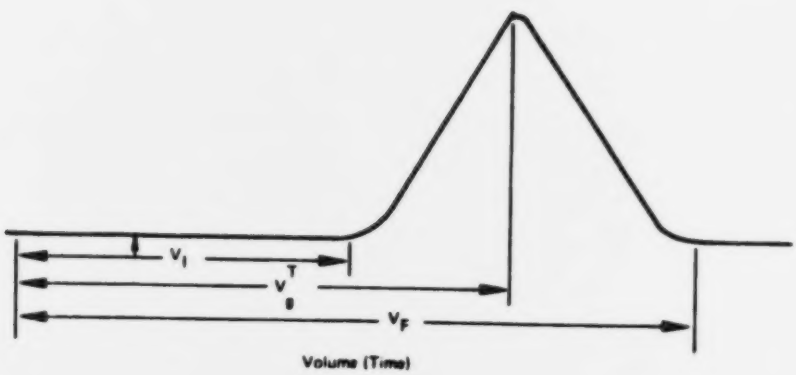


Figure 1. Relationship between Initial Retention Volume V_I and V_g^T

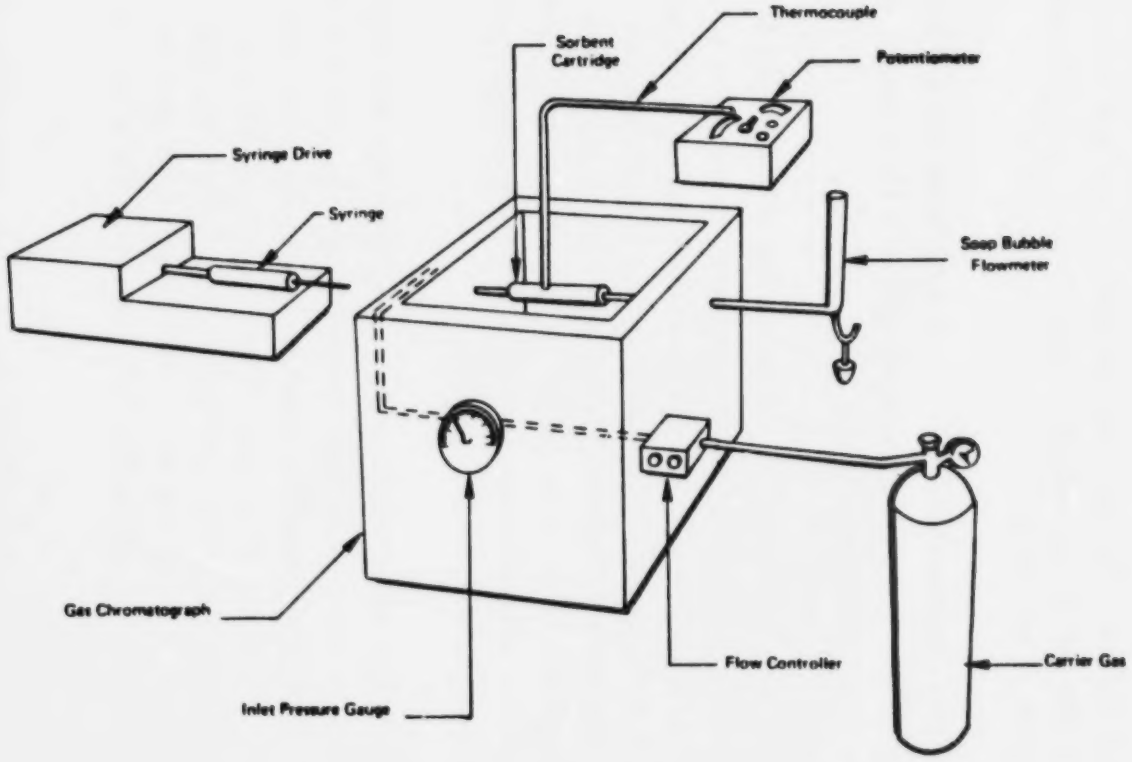


Figure 2. Gas Chromatographic Apparatus Used to Determine V_g^T

0.64 cm x 0.16 cm (1/4 in x 1/16 in) reducing unions drilled out to minimize dead volume. The resin was retained in the trap by stainless steel frits at the end of the tubing. Connections to the chromatograph were made with 0.16 cm tubing.

The gas chromatograph employed in this study was a Varian Model 1200, a single column instrument employing either a flame ionization detector or a photoionization detector.

The column head pressure on the Varian 1200 was read with a U-tube, mercury filled manometer; the pressure reading was taken by puncturing the injection septum with a Hamilton needle, No. 23 gauge conical point with side hole, connected via tygon tubing to the manometer. Flow control was provided by a Brooks Model 8743 flow controller. The retention volume data were collected at maximum electrometer sensitivity and recorded on a Linear Instruments Model 355 potentiometric recorder or a Hewlett Packard Model 7133A recorder.

The column temperatures were measured with the aid of a Rubicon potentiometer. Iron-constantan thermocouples (No. 20) were placed in contact with the sorbent cartridge and connected to the potentiometer. To offset the effect of a "line" room temperature EMF generating junction, a second thermocouple was connected in series with the oven thermocouple and was immersed in an ice bath. The injector and detector temperature were kept at 250°C. Total gas flow rates were measured using a soap bubble flow meter.

In order to study the effects of the major combustion product, water, on V_g, the apparatus was modified as shown schematically in Figure 3. Considerable effort was involved in devising a system that could generate high humidity atmospheres reproducibly for these studies. The modifications are, therefore, described here in some detail.

A photoionization detector was employed during the water and carbon dioxide effect study. The purpose for the change in detectors was that

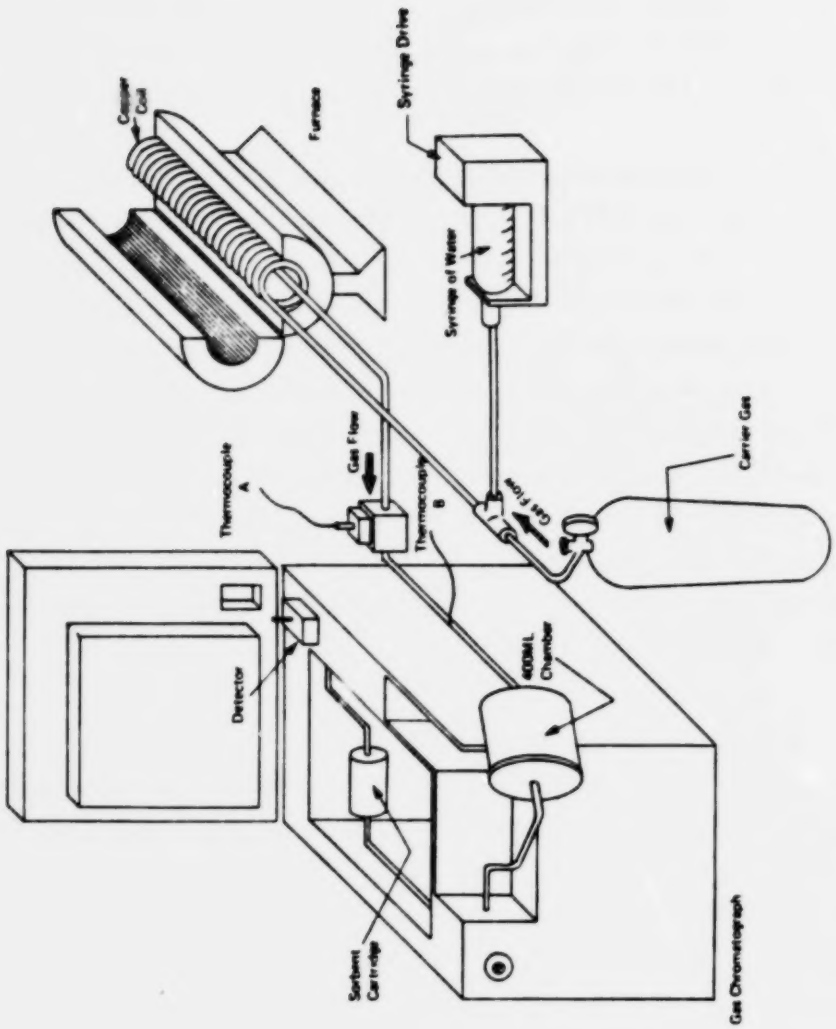


Figure 3. Moisture Generation System

the water vapor caused a noisy flame ionization detector signal in the initial moisture experiments. In order to obtain elution peaks that were discernible from the noise level and still in Henry's Law region, the photoionization detector, which is insensitive to water, was used.

The modifications to the carrier gas system for the study of moisture effects were as follows. The carrier gas line to the Varian 1200 was cut and connected with 0.16 cm (1/16 in) stainless steel swagelok unions at the appropriate inlet and outlet ports. Copper tubing, 0.64 cm (1/4 in. O.D.) was used throughout the humid atmosphere generation system. The tubing went from the inlet of the system to a 0.64 cm (1/4 in) swagelok tee. At this point the liquid water was metered into the system. The method of introducing the water was found to be critically important in achieving reproducible levels. The water was added at 7 mg/min into a 100 mL/min helium carrier gas stream. A 5 cc syringe (Glenco No. 19925-S Gas-Liquid syringe) and a Harvard Apparatus Model 944 infusion-withdrawal pump was used to meter in the water.

The syringe was connected with a plastic union to the tubing. A 6 cm length of 0.16 cm (1/16 in) I.D. plastic tubing was connected with a 0.16 cm (1/16 in) I.D. stainless steel swagelok union to a 70 cm length of 0.16 cm (1/16 in) I.D. high volume stainless steel tubing. The tubing was then placed into the 0.64 cm (1/4 in) tee with the appropriate adapters. The tubing was placed inside the tee to allow the helium to blow by the existing liquid. A fine mesh stainless steel screen was placed at the outlet of the tee to ensure evaporation of all the droplets. From the tee the water/helium mixture went through 6 meters (19 ft) of 0.64 cm (1/4 in) coiled copper tubing enclosed in a tube furnace. From the furnace the carrier gas went into a 400 mL chamber to assure proper mixing. From the chamber, .64 cm (1/4 in) copper tubing was used to the outlet of the system where a 0.16 cm (1/16 in) to 0.64 cm (1/4 in) swagelok reducing union was used to connect the tubing to the carrier gas lines and then to the injection port.

Heating tapes were used on all exposed tubing from the system inlet to the injector port of the gas chromatograph. The gas temperature in the humid atmosphere generation system was maintained above 100°C to avoid condensation of the water, and was monitored by thermocouple A and the thermocouple B. The tube furnace maintained the copper coil at 230°C to ensure all the water was vaporized.

The exact concentration of the water in the carrier stream was measured by determining the flow of the dry carrier gas and then determining the weight of the water per minute. This was done by collecting the water on two cartridges in series filled with Drierite for a known time and determining the water by weight difference. These values were then corrected for the chromatographic conditions used.

C. Introduction of Sorbate Samples

The sample introduction technique used in the elution analysis studies consisted of taking up a small amount (<0.5 μL) of liquid sorbate in a 10 μL syringe, then expelling the liquid and pumping the syringe 50 or more times. This allowed generation of a reproducible dilute sorbate vapor concentration. With the resulting low concentration samples (<10 ppm) the experiments could be conducted in the Henry's Law region.

Three to five replicate elution experiments were run for each set of chromatographic conditions.

D. Materials and Reagents

The helium used in the "other sorbents" study and in the moist atmosphere effects study was prepared by Linde, a Division of Union Carbide, and obtained through Welders Supply of Billerica, Mass.

The carbon dioxide in helium used in the carbon dioxide effects studies was 10.5% carbon dioxide in helium, certified standard, obtained from Matheson Gas Products.

The sorbates used and suppliers are given in Table 1.

TABLE 1

SORBATES AND SUPPLIERS USED IN THE STUDY

Sorbate	Supplier
Pentane	Burdick and Jackson
Hexane	Burdick and Jackson
Decane	Poly Science Corporation
Ethyl Bromide	Fisher
2-Butanone	Poly Science Corporation
Ethylbenzene	Poly Science Corporation
Ethanol	Gold Shield
n-Butanol	Poly Science Corporation

The sorbents and suppliers are given in Table 2.

TABLE 2

SORBENTS AND SUPPLIERS USED IN THE STUDY

Sorbent*	Supplier
Tenax-GC	Applied Science Laboratories
XAD-2	Rohm and Haas
XAD-8	Rohm and Haas
Ambersorb 340	Rohm and Haas
Ambersorb 347	Rohm and Haas
Silica Gel	Davison
Charcoal Lot 104	SKC, Inc.
Charcoal Lot 106	SKC, Inc.

The Tenax-GC and charcoals were used as received. The silica gel was held at 110° for 24 hours to activate it, then stored in a desiccator. The resins obtained from Rohm and Haas were cleaned by several rinses with water then extraction with methanol for 24 hours then methylene chloride extraction for the same period. They were then dried under a nitrogen stream.

*A third Rohm and Haas carbonaceous resin, Ambersorb 348, was not available in time to be included in this study.

E. Matrix of Experiments

Table 3 lists experiments carried out to evaluate the effect of combustion gases and Table 4 lists experiments to study other sorbents for collection of volatile and polar species.

Sorbates were selected to represent the classes of compounds which had major differences in elution behavior. The sorbate compound classes chosen were the aliphatic hydrocarbons and the alcohols. The Kiselev classification[6] for the aliphatic hydrocarbons is Group A (non-polar) and for the alcohols is Group D (highly polar). Specific compounds were chosen to have a short retention time (3 to 10 min) at a given temperature.

In the combustion gas study, experiments that were to be run at higher temperatures (150°) employed sorbates having higher boiling points (greater retention volumes) than those employed in the experiments run at low temperatures (50°C). This was done to provide conveniently measurable retention times run at both low and high relative humidity under constant conditions of 10% moisture in the carrier gas stream.

TABLE 3

EXPERIMENTAL MATRIX - COMBUSTION GAS STUDIES

Analyte	Dry	Moisture (10%)		10% Moisture & CO_2
		Low R.H. (High Temp.)	High R.H. (Low Temp.)	
n-Butanol	X	X	N.T.	N.T.
Ethyl benzene	X	X	N.T.	N.T.
Decane	X	X	N.T.	N.T.
Pentane	X,T	N.T.	X,T	X,T
2-Butanone	X,T	N.T.	X,T	N.T.
Ethanol	X,T	N.T.	X,T	X,T
Ethly Bromide	X,T	N.T.	X,T	N.T.

* X indicates experiments conducted using XAD-2 resin.

T indicates experiments using Tenax-GC resin.

N.T. indicates experiment not performed.

TABLE 4

EXPERIMENTAL MATRIX - OTHER SORBENT STUDIES

	Pentane	Hexane	Ethanol	Butanone
Charcoal - Lot 104	✓	✓	✓	✓
Charcoal - Lot 106	✓	✓	N.T.	✓
Silica Gel	✓	✓	N.T.	N.T.
Ambersorb - 340	✓	✓	✓	N.T.
Ambersorb - 347	✓	N.T.	N.T.	N.T.
XAD-8	✓	✓	✓	✓

✓ = indicates sorbent and sorbate combination tested.

N.T. = indicates combination not tested.

V. RESULTS

A. Effects of Major Combustion Gases

The purpose of these experiments was to determine the effects that typical concentration levels of major flue gas components (water and carbon dioxide) would have on the volumetric breakthrough capacity. The experiments were conducted by adding 10% by volume of carbon dioxide and/or 10% by volume of moisture to the carrier gas in the elution chromatography experiments.

1. Effects of Moisture

In the study of the effects of moisture on retention volume, the carrier gas was maintained at 10% (vol/vol) moisture. Variation of the column oven temperature, keeping the moisture constant at 10% (vol/vol), changed the percent relative humidity (% R.H.). To assist in interpretation of these results, the relationship between % R.H., and column oven temperature at the constant moisture level, is given below in Table 5.

TABLE 5

% RELATIVE HUMIDITY COMPARED TO COLUMN TEMPERATURE AT CONSTANT 10% MOISTURE (vol/vol)

Column Temperature (°C)	% Relative Humidity
140	3.02
120	5.51
100	10.79
80	23.09
50	88.64
20	Saturated

a. Effects of 10% (vol/vol) Moisture - Low % R.H.

The experiments at 10% (vol/vol) moisture--low % R.H. were run only on XAD-2.

The three sorbates used and their Kiselev classification are:

Decane--Group A, Ethyl benzene--Group B, and n-Butanol--Group D. The sorbates were run at both wet and dry conditions for the comparison of the V_g's. The chromatographic conditions and retention volumes determined are given in Table 6.

TABLE 6

COMPARISON OF Vg FOR DRY AND LOW % RELATIVE HUMIDITY ATMOSPHERES IN XAD-2

Sorbate	Column Temperature °C	% Moisture (vol/vol)	% Relative Humidity	Vg (mL/g)
n-Butanol	154.2	10.6	2.3	56.0
	154.0	0	0	56.6
	138.3	10.6	3.5	93.4
	138.1	0	0	97.6
Ethyl benzene	154.2	10.6	2.3	306
	154.0	0	0	308
	138.3	10.6	3.5	618
	138.1	0	0	638
Decane	154.2	10.6	2.3	1320
	154.0	0	0	1370
	138.3	10.6	3.5	3410
	138.1	0	0	3430

The retention volumes are essentially the same for the dry and humid atmosphere for each of the sorbents tested.

b. Effects of 10% (vol/vol) Moisture - High % R.H.

In the 10% (vol/vol) moisture--high % R.H., experiments, two sorbents, XAD-2 and Tenax-GC, and four sorbates, Pentane, 2-Butanone, Ethyl bromide and Ethanol, were used.

The sorbates' Kiselev classifications are: Pentane--Group A,

2-Butanone and Ethyl bromide--Group B, and Ethanol--Group D. The Group A and D compound classifications bracket all the other compound groups except acids; therefore, any significant effect of moisture on retention volume of any compounds except acids would be observed. The ketones and halogenated hydrocarbons, both Group B compounds, were of particular interest because there had been differences of 3-5 kcal/mole between their differential heats of absorption, ΔH_A, on Tenax-GC and XAD-2.

The data obtained with XAD-2 are summarized in Table 7.

TABLE 7

COMPARISON OF V_g's FOR SORBATES AT TWO DIFFERENT RELATIVE HUMIDITIES ON XAD-2

Condition / Sorbate	Column Temperature (°C)	% Moisture (vol/vol)	% Relative Humidity	V_g (mL/g)	Relative V_g wet/dry
Pentane	53.1	0	0	1080	-
	53.2	10.9	87	1090	1.00
2-Butanone	53.1	0	0	3430	-
	53.5	9.8	76	2840	0.83
Ethanol	53.1	0	0	280	-
	54.0	10.8	82	244	0.87
Ethyl bromide	55.0	0	0	640	-
	54.1	11.0	83	615	0.96

Comparing the relative V_g value, there is little effect from the humid atmosphere for pentane and ethyl bromide. There is, however, a 13% decrease in V_g for ethanol and a 17% decrease for 2-Butanone at the higher relative humidity. The results for the 2-Butanone were confirmed in a replicate experiment.

The data obtained for Tenax-GC are given in Table 8. A comparison of the wet and dry atmosphere retention volumes show decreases of 22% for ethyl bromide and ethanol, 31% for 2-Butanone and 43% for pentane. The effects of humidity on Tenax-GC retention volume are much higher than

TABLE 8

COMPARISON OF V_g's FOR SORBATES AT TWO DIFFERENT RELATIVE HUMIDITIES ON TENAX-GC

Condition / Sorbate	Column Temperature (°C)	% Relative Humidity	% H_2O	V_g (mL/g)	Relative V_g $\frac{wet}{dry}$*
Pentane	55.5	0	0	536.9	0.57
	54.4	0	0	532.4	
	54.8	83	11	313.7	
	54.4	78	10	295.5	
Ethyl bromide	55.5	0	0	704.0	0.78
	54.4	0	0	688.8	
	54.8	83	11	582.0	
	54.4	78	10	510.5	
2-Butanone	55.2	0	0	3234.9	0.69
	54.4	0	0	3134.2	
	54.8	83	11	2420.5	
	54.4	78	10	1976.9	
Ethanol	55.5	0	0	233.1	0.78
	54.4	0	0	268.3	
	54.8	83	11	205.6	
	54.4	78	10	186.3	

* Relative V_g, $\frac{wet}{dry}$, determined by taking the average wet V_g over the average dry V_g for a given sorbent.

were found on XAD-2. The difference in moisture sensitivity between the two resins can be understood in view of the more polar nature of Tenax-GC.

2. Effects of Carbon Dioxide

Pentane--Group A and Ethanol--Group D were the sorbates used in determining the effects of carbon dioxide on retention volume. The carbon dioxide experiments were carried out in the presence of 10% (vol/vol) moisture and the results of the combined carbon dioxide/water experiments were compared to the 10% (vol/vol) moisture results. The data are given in Table 9 for both XAD-2 and Tenax-GC.

Comparing the relative V_g with and without carbon dioxide on the XAD-2 shows no sigifnicant change in the retention volume.

In conclusion for XAD-2, introduction of water vapor led to V_g reductions of 0-4% for the nonpolar sorbates and 13-17% for the two polar sorbates. Carbon dioxide at 10% (vol/vol) levels resulted in essentially no further decrease on this sorbent. On the Tenax-GC, a 43% reduction in the retention volume was observed for the addition of moisture and an additional decrease of retention volume of 25% was observed in the combined atmosphere of moisture and carbon dioxide.

B. Comparison of Various Sorbents

The purpose of these experiments was to characterize several sorbents, other than XAD-2 and Tenax-GC, that have been used or have potential for use in sampling applications. One objective was to identify sorbents that would be more effective than XAD-2 or Tenax-GC for collection of very volatile (b.p. <100°C) organic species.

A petroleum base charcoal, a coconut shell base charcoal, silica gel, Ambersorb XE-340, Ambersorb XE-347, and XAD-8 were other solid sorbents investigated. Specific surface area analysis to characterize these sorbents was performed by Micromeritics on the XAD-8, XE-340,

TABLE 9

COMPARISON DATA FOR V_g IN HUMID ATMOSPHERES WITH AND WITHOUT CARBON DIOXIDE

XAD-2

Sorbate \ Condition	Column Temp (°C)	Atmosphere	% Relative Humidity	V_g (mL/g)	Relative V_g* (with CO_2/ without CO_2)
Pentane	53.0	$CO_2 + H_2O$	88.9	1100.7	0.927
	52.5	$CO_2 + H_2O$	91.6	1043.8	
	53.1	H_2O	90.3	1032.5	
	52.6	H_2O	90.4	1281.5	
Ethanol	53.0	$CO_2 + H_2O$	88.9	240.7	1.021
	52.6	$CO_2 + H_2O$	91.6	229.6	
	53.1	H_2O	90.3	210.5	
	52.6	H_2O	90.4	250.0	

Tenax-GC

Pentane	52.1	$CO_2 + H_2O$	93.4	345.1	0.752
	52.6	$CO_2 + H_2O$	90.3	304.1	
	52.8	H_2O	82.2	464.9	
	52.8	H_2O	88.4	398.2	
Ethanol	52.1	$CO_2 + H_2O$	93.4	167.2	0.877
	56.6	$CO_2 + H_2O$	90.3	185.3	
	52.8	H_2O	82.2	204.6	
	52.8	H_2O	88.4	197.3	

*Relative V_g $\frac{\text{with } CO_2}{\text{without } CO_2}$ determined by taking average $CO_2 + H_2O$ V_g over H_2O V_g for a given sorbent.

XE-347, charcoal Lot 104, and charcoal Lot 106. The data are given in Appendix A. The sorbates used and their Kiselev classification are Pentane and Hexane--Group A, and Ethanol and n-Butanol--Group D. In the previous work, a correlation between Log V_g^{20} and boiling point of the compounds in chemical classes was determined. In this screening of other sorbents, there were not enough data points per sorbent and sorbate class to quantitatively compare the correlation between V_g and a physical property of the sorbate.

Results of the individual experiments are presented in the next four parts. A comparison of all of the sorbents is given in part 5.

1. Charcoals

The charcoals used were SKC, Inc., Lot 104, a petroleum-based charcoal, and Lot 106, a coconut shell based charcoal. These charcoals, Type I according to the Kiselev scheme for sorbents,[7] are a non-specific type of sorbent with surface areas of 1270 m^2/g, Lot 104, and 1270 m^2/g, Lot 106. The experimental data is summarized in Table 10.

In Table 11 the sorbate retention volumes, V_g, are compared at a common temperature. The retention volumes on the Lot 106, coconut shell base charcoal, are almost a factor of 2 greater than the V_g's on the Lot 104, petroleum base charcoal.

2. Silica Gel

The silica gel used was Davison Grade 5. This sorbent is classified by Kiselev as Type II, Specific, with localized positive charge. The silica gel can be described as a highly polar sorbent.

The experimental results using silica gel are reported in Table 12. Results could not be obtained for alcohols because they exhibited excessive peak broadening, and it is therefore recommended that silica gel not be used for sampling of alcohols.

TABLE 10

RETENTION VOLUMES, V_g, ON CHARCOALS LOTS 104 AND 106
FOR THE TESTED SORBATES

Sorbent	Compound	Column Temp. °C	V_g (mL/g)	Standard Deviation
Charcoal Lot No. 104	Pentane	263.0 278.6	699 467	7.7 4.6
	Hexane	262.8 278.6	3,350 2,060	29.1 18.7
	Ethanol	240.2 257.6	137 88.9	3.0 3.2
	n-Butanol	252.0 263.0	205 153	8.2 7.5
Charcoal Lot No. 106	Pentane	263.3 278.1 279.2	1,150 782 769	9.7 7.0 8.3
	Hexane	269.2 278.1	4,490 3,520	75.4 17.4
	Ethanol	262.8 271.3	307 278	7.9 3.4
	n-Butanol	263.3 279.2	238 177	4.2 4.0

TABLE 11

COMPARISON OF RETENTION VOLUME, V_g, OF THE CHARCOALS LOTS 104 AND 106 AT COMMON TEMPERATURES

		Lot 104	Lot 106
Compound	Interpolation Temp. °C	V_g(mL/g)	V_g(mL/g)
Pentane	270°	581	964
Hexane	270°	2,680	4,390
n-Butanol	260°	165	254
Ethanol	260°	87.7	318

TABLE 12

RETENTION VOLUMES, V_g, ON SILICA GEL FOR THE TESTED SORBATES

Sorbent	Compound	Column Temp.°C	Vg(mL/g)	Standard Deviation
Silica Gel	Pentane	73.4 81.8	87.4 46.7	5.7 5.7
	Hexane	94.5 108.9	92.3 54.9	11 5.5

3. Ambersorb XE-340 and XE-347

The Ambersorb XE-340 is a non-polar sorbent with a surface area of 480 m^2/g. The Ambersorb XE-347 is a polar sorbent with a surface area of 457 m^2/g. The experimental results are reported in Table 13.

One sorbate, pentane, was tested on the Ambersorb XE-347. Comparing the retention volume data from Table 14 of the pentane on the XE-347 with corresponding data for the charcoals and XE-340, indicated that the XE-347 was similar to the XE-340 and charcoals. Further studies to explore possible subtle differences among these high V_g sorbents due to, for example, polarity differences, were beyond the scope of this work.

4. XAD-8

Amberlite XAD-8, an acrylic ester, is a polymeric resin with a surface area of 120 m^2/g. The data for the XAD-8 experiments are given in Table 15. From the data in Table 14, the XAD-8 behaves much like XAD-2 and Tenax-GC for non-polar compounds, but has a slightly larger affinity (factor of ten) for alcohols.

5. Comparison of V_g and K_A Values Among Sorbents

In Table 14, calculated retention volume values have been presented for the sorbates on the six sorbents at 20°C. Because of the large extrapolation (270°C to 20°C) required for some of the sorbents, the data should be compared primarily with a view to order of magnitude differences and effects. The extrapolated values are compared to the previously reported retention volumes of the sorbates on Tenax-GC and XAD-2.

Comparing the retention volumes of the charcoals to those of Tenax-GC and XAD-2, the charcoal retention volumes are 10^4 to 10^5 times larger for alcohols. From the data, the two charcoals behave very similarly in their activity. Ambersorb XE-340 and XE-347 are roughly comparable to the charcoals tested. Silica gel behaves very similarly to the polymeric resins, XAD-2 and Tenax-GC for the aliphatic hydrocarbons.

TABLE 13

RETENTION VOLUMES, V_g, ON THE AMBERSORBS XE-340 AND XE-347 FOR THE TESTED SORBATES

Sorbent	Compound	Column Temp. °C	V_g (mL/g)	Standard Deviation
Ambersorb XE-340	Pentane	178.8	490	7.3
		187.9	274	6.7
	Hexane	178.8	1710	154
		196.8	716	108
	Ethanol	196.8	193	6.9
		207.0	152	59
Ambersorb XE-347	Pentane	245.3	1680	80
		254.3	1270	25

TABLE 14

Comparison of Sorbents via the Retention Volumes (V_g) of the Selected Sorbates at 20°C

Sorbent / Sorbate	Charcoal Lot 104	Charcoal Lot 106	Silica Gel	Amberserb XE-340	Amberserb XE-347	XAD-8	XAD-2	Tenax-GC
Pentane	1×10^8	1×10^8	1×10^4	4×10^9	2×10^8	3×10^4	2×10^{4}**	2×10^{3}**
Hexane	4×10^9	2×10^9	3×10^3	4×10^8	--	3×10^4	8×10^{4}**	1×10^{4}**
Ethanol	3×10^6	6×10^4	—	2×10^5	—	2×10^4	2×10^{3}*	9×10^{2}*
n-Butanol	2×10^7	1×10^6	—	—	—	2×10^5	2×10^{4}*	4×10^{4}*

* From EPA Report EPA-600/7-78-054, pages 22-23.

** Values determined from linear regression equations reported in EPA-600/7-78-054, pages 52-53.

TABLE 15

RETENTION VOLUMES ON XAD-8 OF THE TESTED SORBATES

Sorbent	Compound	Column Temp. °C	Vg(mL/g)	Standard Deviation
XAD-8	Pentane	96.9	103	2.1
		87.9	174	3.4
	Hexane	103.4	268	3.4
		114.4	164	0
	Ethanol	114.4	108	1.3
		126	66.2	3.3
	n-Butanol	138.5	245	2.5
		147.3	173	4.0

Comparing the retention volumes of the charcoals to those of Tenax-GC and XAD-2, the charcoal retention volumes are 10^4 to 10^5 times larger for alcohols. From the data, the two charcoals behave very similarly in their activity. Ambersorb XE-340 and XE-347 are roughly comparable to the charcoals tested. Silica gel behaves very similarly to the polymeric resins, XAD-2 and Tenax-GC for the aliphatic hydrocarbons. The retention volumes for alcohols on XAD-8 is a power of ten larger than XAD-2 and 100 times larger for Tenax-GC.

In order of decreasing volumetric capacity, the sorbents screened are: Charcoal Lot 104 $\geq$ Charcoal Lot 106 > Ambersorb XE-340 > Ambersorb XE-347 > XAD-8 > XAD-2 > Tenax-GC.

The equilibrium adsorption coefficient, K_A, can be calculated from the retention volume data in Table 14 and the specific surface Area, A_s°, for each of the sorbents used. In Table 16, the specific surface area for the sorbents are given. K_A is a measure of the intrinsic thermodynamic affinity of sorbent for sorbate, independent of effects of increased surface area. The equation is:

$$K_A = \frac{V_g}{A_s^\circ RT}$$

where: V_g = retention volume at 20°C in mL/g
A_s° = specific surface area in m^2/gram
$R = 6.232 \times 10^4$ mL-mm/mole - °K
T = temperature of V_g (293.16°K) of V_g value

The absorption coefficients have been calculated with the retention volume data from Table 14 and listed in Table 17. It is interesting to note that the charcoals, Lots 104 and 106, and Ambersorbs XE-340 and 347, both non-specific/non-polar, have greater K_A's (by three to five orders of magnitude) than the polymeric resins, XAD-2, XAD-8, and Tenax-GC when comparing pentane and hexane as the sorbates. When using

TABLE 16

SPECIFIC SURFACE AREAS, A_s°, FOR SORBENTS

Sorbent	BET Surface Area (m^2/g)
XAD-2	364
Tenax-GC	23.5
XAD-8	120
Ambersorb XE-340	480
Ambersorb XE-347	457
Charcoal Lot 104	1270
Charcoal Lot 106	1270

TABLE 17

Adsorption Coefficients*, K_A, on Resins at 20°C

Sorbent / Sorbate	Charcoal Lot 104	Charcoal Lot 106	Ambersorb XE-340	Ambersorb XE-347	XAD-8	XAD-2	Tenax-GC
Pentane	4×10^{-3}	4×10^{-3}	5×10^{-1}	2×10^{-7}	1×10^{-5}	3×10^{-6}	5×10^{-6}
Hexane	2×10^{-1}	9×10^{-2}	5×10^{-2}	—	1×10^{-5}	1×10^{-5}	2×10^{-5}
Ethanol	1×10^{-4}	3×10^{-6}	2×10^{-5}	—	9×10^{-6}	3×10^{-7}**	2×10^{-6}**
n-Butanol	9×10^{-4}	4×10^{-5}	—	—	9×10^{-5}	3×10^{-6}**	1×10^{-4}**

* In units of moles/mm-m^2

** From EPA Report EPA-600/7-78-054, page 71

the alcohols ethanol and n-Butanol for comparison, the absorption coefficients are also greater for the carbonaceous sorbents than for the other resins. However, the K_A's for the alcohols vary over a smaller range (one to three orders of magnitude) than those for the alkanes.

Sorbent attraction, in order of decreasing intrinsic affinity (K_A) for sorbates tested, are: Charcoal Lot 104 > Ambersorb XE-340 > Charcoal Lot 106 > Ambersorb XE-347 > XAD-8 > Tenax-GC > XAD-2.

VI. CONCLUSIONS AND RECOMMENDATIONS

In this work, elution chromatography was successfully used to study the effects of combustion gases, carbon dioxide, water and the combined effect of carbon dioxide and water, on the retention volume of trace level sorbates on XAD-2 and Tenax-GC. The retention behavior of XAD-2 is relatively unaffected by the combustion gases studied. Introduction of water vapor led to V_g reductions of 0-4% for the non-polar sorbates studied and 13-17% for the two polar sorbates. Carbon dioxide at 10% (vol/vol) levels resulted in essentially no further decrease for XAD-2. On the other hand, the V_g values on Tenax-GC were reduced by 22-43% in the presence of water vapor, and an additional 25% decrease was observed when carbon dioxide was introduced.

Other sorbents have been investigated for collecting of volatile and polar organics. The charcoals, Lot 104 and Lot 106, and the Ambersorbs, XE-340 and XE-347, appear to be potential candidates for this purpose. The charcoals and Ambersorbs show V_g values three to five orders of magnitude higher than XAD-2 for non-polar sorbates. For alcohols, the differences are one to three orders of magnitude. The increased V_g's are only partially attributable to differences in surface area. Based on this study, the order of preference in selection of sorbents for collection of high volatile and polar organics, listed in order of decreasing intrinsic affinity (K_A), are: Charcoal Lot 104 > Ambersorb XE-340 > Charcoal Lot 106 > Ambersorb XE-347 > XAD-8 > Tenax-GC > XAD-2.

Further studies with sorbents should include:

1. The recovery of various chemical classes from different sorbents: XAD-2, Ambersorb XE series and charcoals.
2. Determining retention volumes for organometallic species on XAD-2 and Tenax-GC.
3. Further investigation of a sorbent to collect volatile organics.

VII. REFERENCES

1. Adams, J.W., K.T. Menzies, and P.L. Levins, "Selection and Evaluation of Sorbent Resins for Collection of Organic Compounds," EPA Report 600/7-77-044, April, 1977, PB 268-559.

2. Gallant, R.J., J. King, P. Levins, J. Piecewicz, "Characterization of Sorbent Resins for Use in Environmental Sampling," EPA Report 600/7-78-054, March, 1978, PB 284-347.

3. Hamersma, J.W., S.L. Reynolds, and R.F. Maddalone, "IERL-RTP Procedures Manual; Level 1 Environmental Assessment," EPA Report 600/2-76-160a, June, 1976, PB 257-850.

4. Locke, D.C., Physiochemical Measurements Using Chromatography in "Advances in Chromatography," Vol. 14, J.C. Gidding, E. Grushka, J. Cazes, and P.R. Brown, eds., Marcel Dekker, Inc., 1976, pp. 87-198.

5. Kobayaski, R., H.A. Deans and P.S. Chappelear, Physio-Chemical Measurements by Gas Chromatography, in "Applied Thermodynamics," American Chemical Society, Washington, D.C., 1968, pp. 227-246.

6. Kiselev, A.V. and Y.I. Yashin, "Gas-Adsorption Chromatography," Plenum Press, N.Y., 1969, pp. 11-14.

APPENDIX A

Incremental Surface Area Distribution

Figure A-1. Incremental Surface Area Distribution (Desorption) XE-340

Figure A-2. Incremental Surface Area Distribution (Desorption) XE-347

SAMPLE:ARTHUR D. LITTLE XE-347 STA: 3 EQTIME: 3 MODE: 5 METHOD: 3

INCREMENTAL SURFACE AREA DISTRIBUTION (DESORPTION)

% OF MAXIMUM SURFACE AREA(+14.097 SQ M/G)
VERSUS AVERAGE PORE DIAMETER, ANGSTROMS

```
                20%          40%          60%          80%          100%
    I.....I.....I.....I.....I.....I.....I.....I.....I.....I.....I
+22.5 **************************************************************
+27.5 *********************************
+32.5 **********
+37.5 **********
+42.5 ********
+47.5 **
+52.5
+57.5 *
+62.5 **
+67.5 *
+72.5 **
+77.5 **
+82.5 *
+87.5 *
+92.5 ***
+97.5
+105.0 ***
+115.0 ********
+125.0 ******
+135.0 *****
+145.0 ***********
+155.0 *******
+170.0 ************************
+190.0 ****************************
+210.0 ***************************
+230.0 ************************************
+250.0 ******************************
+270.0 ******************
+290.0 ***********
+325.0 ***************
+375.0 **
+425.0
+475.0
+550.0
```

Figure A-3. Incremental Surface Area Distribution (Desorption) XAD-8

Figure A-4. Incremental Surface Area Distribution (Desorption)
Charcoal Lot 104

Figure A-5. Incremental Surface Area Distribution (Desorption)
Charcoal Lot 106